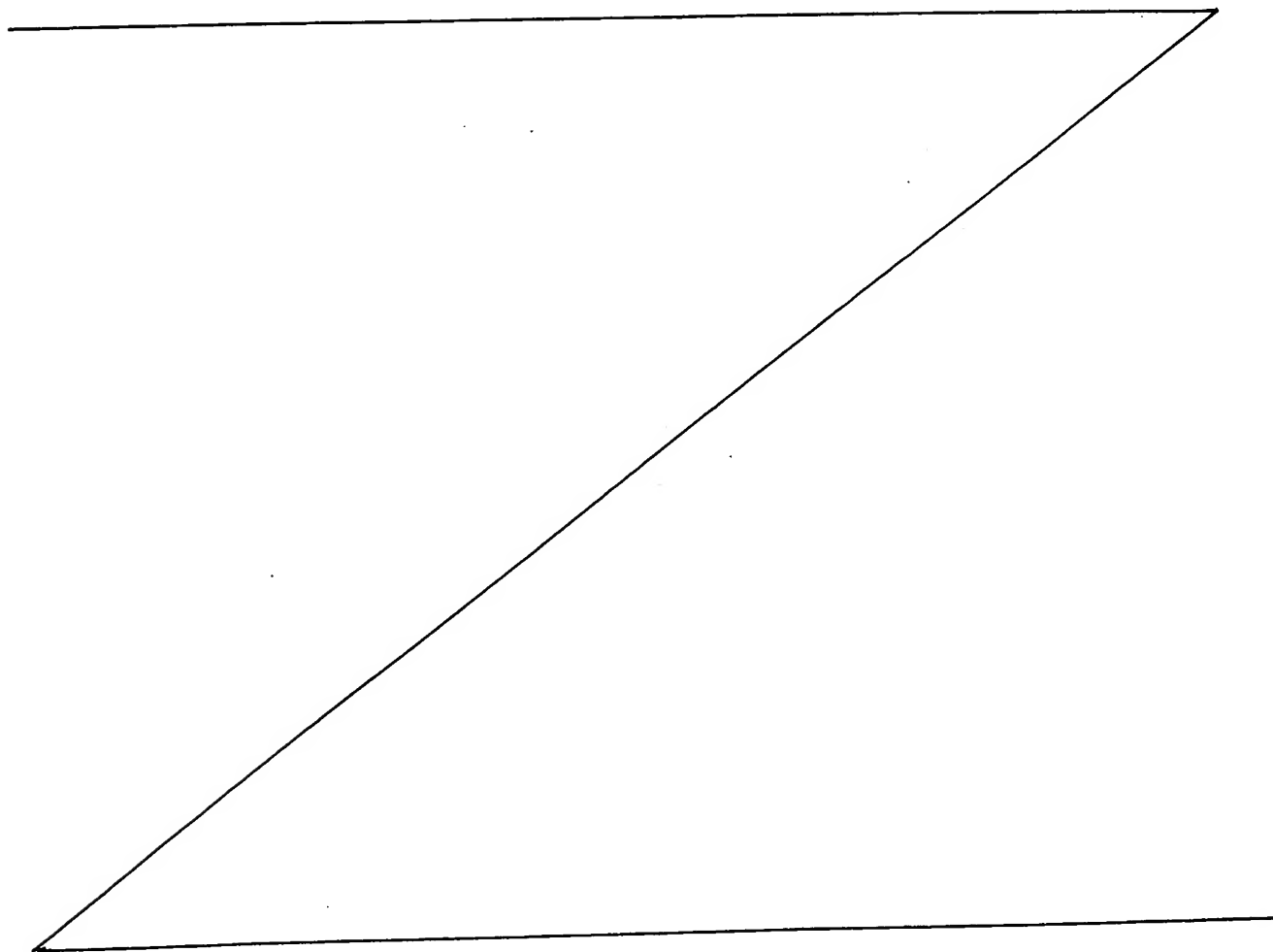


CROSS REFERENCE TO RELATED APPLICATIONS

This application is a continuation of Application No. 08/583,009, filed September 5, 1993, which is the U.S. National Stage of International Application No. PCT/NL93/00181, filed September 6, 1993. The entire disclosure of Application No. 08/583,009 is considered as being part of the disclosure of this application, and the entire disclosure of Application No. 08/583,009 is expressly incorporated by reference herein in its entirety.

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1 TONER PARTICLES WITH MODIFIED CHARGEABILITY

2 1A5 B1 FIELD OF THE INVENTION

3 This invention relates to the field of electrostatic
4 imaging and, more particularly, to the preparation of liquid
5 toners containing components for imparting chargeability to
6 ordinarily unchargeable liquid toner particles, enhancing
7 the chargeability of insufficiently chargeable liquid toner
8 particles, and controlling the polarity of liquid toner
9 particle charge.

10 BACKGROUND OF THE INVENTION

11 In the art of electrostatic photocopying or photo-
12 printing, a latent electrostatic image is generally produced
13 by first providing a photoconductive imaging surface with a
14 uniform electrostatic charge, e.g. by exposing the imaging
15 surface to a charge corona and then selectively discharging
16 the surface by exposing it to a modulated beam of light
17 corresponding, e.g., to an optical image of final image to
18 be produced. This forms a latent electrostatic image having
19 a "background" portion at one potential and a "print"
20 portion at another potential. The latent electrostatic image
21 can then be developed by applying to it charged pigmented
22 toner particles, which adhere to the print portions of the
23 photoconductive surface to form a toner image which is
24 subsequently transferred by various techniques to a final
25 substrate (e.g. paper).

26 It will be understood that other methods may be
27 employed to form an electrostatic image, such as, for
28 example, providing a carrier with a dielectric surface and
29 transferring a preformed electrostatic charge to the
30 surface. The charge may be formed from an array of
31 styluses. It is to be understood that the invention is
32 applicable, generally to both printing and copying systems.

33 In liquid-developed electrostatic imaging, the toner
34 particles are usually dispersed in an insulating non-polar
35 liquid carrier such as an aliphatic hydrocarbon fraction,
36 which generally has a high-volume resistivity above 10^9 ohm
37 cm, a dielectric constant below 3.0 and a low vapor pressure
38 (less than 10 torr. at 25°C). The liquid developer system

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1 further comprises so-called charge directors, i.e. compounds
2 capable of imparting to the toner particles an electrical
3 charge of the desired polarity and uniform magnitude.

4 In the course of the process, liquid developer is
5 applied to the photoconductive imaging surface. Under the
6 influence of the electrical potential present in the latent
7 image and a developing electrode which is usually present,
8 the charged toner particles in the liquid developer migrate
9 to the print portions of the latent electrostatic image,
10 thereby forming the developed toner image.

11 Charge director molecules play an important role in
12 the above-described developing process in view of their
13 function of controlling the polarity and magnitude of the
14 charge on the toner particles. The choice of a particular
15 charge director for use in a specific liquid developer
16 system, will depend on a comparatively large number of
17 physical characteristics of the charge director compound,
18 inter alia its solubility in the carrier liquid, its
19 chargeability, its high electric field tolerance, its
20 release properties, its time stability, the particle
21 mobility, etc., as well as on characteristics of the toner
22 and the development apparatus. All these characteristics
23 are crucial to achieve high quality imaging, particularly
24 when a large number of impressions are to be produced.

25 A wide range of charge director compounds for use in
26 liquid-developed electrostatic imaging are known from the
27 prior art. Examples of charge director compounds are ionic
28 compounds, particularly metal salts of fatty acids, metal
29 salts of sulfo-succinates, metal salts of oxyphosphates,
30 metal salts of alkyl-benzenesulfonic acid, metal salts of
31 aromatic carboxylic acids or sulfonic acids, as well as
32 zwitterionic and non-ionic compounds, such as
33 polyoxyethylated alkylamines, lecithin, polyvinyl-
34 pyrrolidone, organic acid esters of polyvalent alcohols,
35 etc.

36 Desired physical characteristics of toner particles is
37 that they have softening points consistent with the
38 temperature capabilities of the final substrate, good

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1 adhesion to the substrate and abrasive resistance. To this
2 end toner particles are often formed of polymer materials
3 having these properties and having pigments dispersed
4 therein or which are otherwise colored.

5 Unfortunately, many polymers which would make ideal
6 toner materials are difficult if not impossible to charge to
7 a level which is useful in an electrostatic imaging process.

8 U.S. Patent No. 4,526,852 (Herrmann et al) used a
9 particulate acid or ester wax derived from montan wax,
10 hydrated castor oil or polyoctadecene to reduce the specific
11 electrical conductivity of a liquid developer containing
12 negatively charged toner particles.

13 Notwithstanding the undoubted utility of charge
14 directors, and the various attempts which have been made to
15 improve their performance, from one aspect their use depends
16 on the toner particles having a surface which is receptive
17 to the application of charge directors. In other words, the
18 art would have considered certain types of particles either
19 virtually unchargeable or insufficiently chargeable.
20 Moreover, it may be desirable to change the polarity of the
21 charged particles from that which is conventionally
22 associated with a particular charge director, when used in
23 conjunction with a particular type of toner particle.

24 SUMMARY OF THE INVENTION

25 It is an object of the present invention to provide
26 improved liquid toner compositions containing charge
27 directors, which address the problems mentioned in the
28 preceding paragraph. Other objects of the invention will
29 appear from the description which follows.

30 The present invention accordingly provides in one
31 aspect, a liquid toner for electrostatic imaging which
32 comprises:

- 33 an insulating non-polar carrier liquid;
- 34 at least one charge director; and
- 35 toner particles dispersed in the carrier liquid, the
- 36 particles comprising:
 - 37 a core material which is unchargeable or weakly
 - 38 chargeable by the at least one charge director, but which is

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1 are otherwise suitable for use as a toner material; and
2 a coating of at least one ionomer component in
3 an amount effective to impart enhanced chargeability to the
4 ordinarily unchargeable or weakly chargeable particles.

5 In a second aspect of the invention, there is provided
6 a liquid toner for electrostatic imaging which comprises:
7 an insulating non-polar carrier liquid;
8 at least one charge director; and
9 toner particles dispersed in the carrier liquid, the
10 toner particles comprising:

11 a core material which is chargeable to a first
12 polarity by the at least one charge director; and

13 a coating of at least one ionomer component in
14 an amount effective, together with the at least one charge
15 director, to impart a charge having a polarity different
16 from the first polarity to the coated particles.

17 In a further aspect of the invention, a method of
18 producing liquid toner for electrostatic imaging, which
19 method comprises dispersing particles in an insulating non-
20 polar carrier liquid, and mixing also at least one ionomer
21 with the liquid. Preferably, the mixture is first heated to
22 a temperature at which the ionomer dissolves in the carrier
23 liquid and then cooled to a temperature whereat the ionomer
24 is not soluble in the carrier liquid, thereby coating the
25 particles with ionomer material.

26 In a preferred embodiment of the invention, the
27 mixture is agitated at least during the step of cooling.

28 Preferably, at least one charge director is added to
29 the mixture, most preferably after the step of cooling.

30 According to a preferred embodiment of the invention,
31 the particles are formed of a material which, in the
32 presence of charge director alone, is ordinarily
33 unchargeable or weakly chargeable, but is otherwise suitable
34 for use as toner particles, and the at least one ionomer
35 component is used in an amount effective to impart enhanced
36 chargeability to the toner particles.

37 In a preferred embodiment of the invention, the at
38 least one ionomer component is used in an amount effective

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1 to reverse the polarity conventionally imparted to the
2 material of the particles by the at least one charge
3 director.

4 In still another aspect, the present invention
5 provides an electrostatic imaging process which comprises
6 the steps of: forming a charged latent electrostatic image
7 on a photoconductive surface; applying to said surface
8 charged colorant particles from a liquid toner of the
9 invention (or as prepared by the method of the invention);
10 and transferring the resulting toner image to a substrate.

11 Generally, the ionomers utilized as coatings in the
12 Examples herein are low molecular weight ionomers which are
13 generally considered to be too soft to be used alone for
14 toner materials.

15 BRIEF DESCRIPTION OF THE DRAWINGS

16 The present invention will be understood and
17 appreciated more fully from the following detailed
18 description of the preferred embodiments thereof, taken in
19 conjunction with the drawings in which:

20 Fig. 1 shows the effect of A 291 ionomer used in
21 accordance with an embodiment of the invention on the
22 chargeability of tentacular toner particles;

23 Fig. 2 shows the effect of A 290 ionomer used in
24 accordance with an embodiment of the invention on the
25 chargeability of tentacular toner particles;

26 Fig. 3 shows the effect of both A 290 and A 291 on the
27 mobility of toner particles at 40 °C;

28 Figs. 4 and 5 show electron-micrographs of spherical
29 toner particles in accordance with a preferred embodiment of
30 the invention.

31 DETAILED DESCRIPTION OF THE INVENTION

32 In a particular preferred embodiment of the invention,
33 the toner particles are defined as ordinarily unchargeable,
34 that is to say that they would be regarded as unchargeable
35 by the skilled person, in absence of a knowledge of the
36 present invention, and the ionomer is used in an amount
37 effective to impart chargeability to the toner particles.

38 In another preferred embodiment of the invention, the

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1 toner particles are defined as weakly chargeable, that is to
2 say that although the skilled person would be aware that a
3 weak charge could be imparted to the particles it would be
4 apparent that this property would be of little or no utility
5 so far as practical applications in electrostatic imaging
6 were concerned. In this case, the ionomer is used in an
7 amount effective to impart enhanced chargeability to the
8 toner particles.

9 In yet another preferred embodiment of the invention,
10 the ionomer is used in an amount effective to reverse the
11 polarity known by the skilled person to be conventionally
12 imparted to the toner particles by the at least one charge
13 director. In this connection, for example, resinous toner
14 particles containing carboxylic acid groups would be
15 conventionally expected to be negatively chargeable because
16 of their potential to lose carboxylic hydrogen atoms as
17 protons leaving residual anionic carboxylate groups or to
18 form a salt with potential loss of the cation leaving a
19 carboxylate anion. Conversely, for example, resinous toner
20 particles containing di-amino groups would be conventionally
21 expected to be positively chargeable because of their
22 potential to add protons, forming resin particle-attached
23 quaternary ammonium groups.

24 In yet another preferred embodiment of the invention,
25 the "core" of the particles comprise a pigmented polymer. As
26 is well known in the art, the chargeability of polymer
27 materials is dependent on the pigment used to color the
28 particles. When the particles are coated by an ionomer, or
29 by an uncolored layer of some other chargeable polymer, the
30 chargeability is the same for all colors.

31 The toner particles, insulating non-polar carrier
32 liquids, colorant particles and charge directors, which may
33 suitably be used in the liquid toners and the compositions
34 of the invention may be those known in the art.
35 Illustratively, the insulating non-polar liquid carrier,
36 which should preferably also serve as carrier for the charge
37 directors, is most suitably a hydrocarbon fraction,
38 particularly an aliphatic hydrocarbon fraction, having

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1 suitable electrical and other physical properties. More
2 particularly, the carrier is preferably an insulating non
3 polar carrier liquid hydrocarbon having a volume resistivity
4 above 10^9 ohm-cm and a dielectric constant below 3.0.
5 Preferred solvents are the series of branched-chain
6 aliphatic hydrocarbons and mixtures thereof, e.g. the
7 isoparaffinic hydrocarbon fractions having a boiling range
8 above about 155°C, which are commercially available under
9 the name Isopar (a trademark of the Exxon Corporation).

10 The toner particles may be, e.g., thermoplastic resin
11 particles as is known in the art. Alternatively, the
12 skilled person would be able to select toner particles made
13 from a particulate substance not hitherto regarded as
14 chargeable by the use of charge directors, in relation to
15 electrostatic imaging applications, but whose physical and
16 chemical properties make them otherwise suitable, for the
17 purpose of charging them by use of ionomers and charge
18 directors in accordance with the present invention.

19 The ionomers utilized in a preferred embodiment of the
20 present invention are those which are soluble in the carrier
21 liquid at elevated temperatures and are less soluble at
22 ambient temperatures, so that on mixing the components
23 mentioned hereinbelow including the ionomer, at temperatures
24 above ambient temperatures, the ionomer dissolves in the
25 carrier liquid and then, when cooling the mixture, the
26 ionomer will be deposited as a coating on the toner
27 particles. The ionomers should preferably have a relatively
28 low molecular weight to produce the above referenced
29 solubility characteristics and also to provide a low
30 viscosity.

31 Suitable ionomers for use in the present invention are
32 e.g. those marketed by Allied Signal under the registered
33 Trade Mark "AClyn", which are described as low molecular
34 weight ethylene-based copolymers neutralized with metal
35 salts forming ionic clusters. Examples of these are shown
36 in Table 1.

37 The ionomers listed in Table 1 are based on m t acrylic
38 acid. However, ionomers based on other carboxylic acids or

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1 on other organic acids such as sulfonic and phosphoric acids
 2 are also believed to be useful in the present invention.
 3 Furthermore, non-ethylene based ionomers are also believed
 4 to be useful in the present invention, if they have the
 5 other characteristics defined in the preceding paragraph.

6 Table 1: AClyn Low Molecular Weight Ionomers

Properties:		(1)	(2)	(3)	(4)	(5)
		Acid	Melt		Part.	Low Field
Code	Cation	No.	Point, °C	Viscosity	Cond.	Cond.
201A	Ca	42	102	5,500	65	11
246A	Mg	0	95	7,000	63	17
276A	Na	0	98	70,000	239	23
290	Zn	60	99	900	209	14
291A	Zn	40	102	5,500	304	23
293A	Zn	30	101	500	162	16
295A	Zn	0	99	4,500	116	12

26 Notes to Table 1:

27 (1) in units of mg KOH/g;

28 (2) per ASTM-D 633;

29 (3) cps at 190°C;

30 (4) and (5) conductivity of 1% n.v.s micro-dispersion in
 31 ISOPAR L; The materials were prepared by grinding a 20% non-
 32 volatile solids mixture (in Isopar -L) in an attritor for 24
 33 hours (the resulting particle size is between 0.8 and 1.5
 34 micrometers) and charged with 100mg/g of Lubrizol 890
 35 (Lubrizol Corp.). The high field conductivity is measured at
 36 1.5 V/micrometer (DC) and the low field conductivity (5) at
 37 5 V/mm at 5 Hz. The particle conductivity, (4) is defined as
 38 the difference between the high and low field conductivities
 39 and is a measure of the conductivity of the particles alone
 40 (without the conductivity of the carrier liquid).

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1 Th invention will be illustrated by the following
2 non-limiting Examples.

3 **EXAMPLE 1: TONER CONTAINING CARBOXYLIC COPOLYMER PARTICLES**

4 (a) 7.5 kg of a thermoplastic ethylene/methacrylic
5 acid/isobutyl methacrylate copolymer marketed as Elvax 5650T
6 (E.I. du Pont) and 7.5 kg Isopar L (Exxon) are mixed for one
7 hour at speed 2 in a Ross double planetary mixer (10 gallon
8 LDM) for one (1) hour, at a controlled temperature of 150°C,
9 followed by addition of 15 kg Isopar L preheated at 90°C and
10 further mixing at speed 5 for one (1) hour. The mixture is
11 cooled to room temperature while mixing at speed 3.

12 (b) 10.44 kg of the product of part (a) is transferred
13 to an S-15 attritor (Union Process, Inc., Akron, OH)
14 together with 390 g of FG 7351 cyan pigment, 45 g aluminum
15 stearate and 9.125 kg Isopar L. The mixture is ground for 2
16 hours at speed 6, at 54°C, after which 10 kg Isopar L is
17 added and grinding is effected for a further 38 hours, to
18 produce a dispersion of 1.6 micrometer diameter tentacular
19 particles.

20 (c) The product of part (b) (300 g diluted to 2%
21 n.v.s.) is placed in a vessel, subjected to the action of a
22 Ross Model Lab-ME high shear mixer at room temperature, and
23 an Isopar L solution of 10% by weight ionomer (AClyn 290 or
24 291A, preheated at 115°C, the ionomer constituting either 10
25 or 20% by weight of the toner solids), is slowly added,
26 after which maximum shear is applied for 3 minutes. The
27 dispersion is allowed to equilibrate for 1 hour and then
28 Lubrizol 890 (a polyisobutenyl-succinimide dispersant
29 additive) is added in an amount of 100 mg charge director
30 per gram of toner solids; the product is then allowed to
31 equilibrate for a further 2 hours, after which time the
32 charging parameters are measured. In an alternative
33 procedure in step (c), the initial shear may be conducted
34 e.g. at 40°C instead of room temperature. Results are shown
35 in Figs. 1-3, from which it may be seen that use of the
36 ionomer increases both the particle conductivity and the
37 mobility of the toner particles. Figs. 1 and show the effect
38 of A 290 and A 291 respectively on conductivity and Fig. 3

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1 shows the effect of both materials on conductivity and mobility at 40°C.

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EXAMPLE 2: SPHERICAL TONER PARTICLES

4 (a) Preparation of intermediate dispersed phase.

5 Dynapol S-1228 (120 g) is loaded onto the rolls of a
6 Brabender 2-roll mill preheated by an oil heating unit to
7 100°C, and aluminum tristearate (2.4 g) and blue pigment BT
8 583D (30 g) are added thereto, at a speed of 60 rpm and a
9 torque of 40 Nm. After about 20 minutes the material is
10 discharged and shredded into small pieces.

11 (b) Preparation of caramel.

12 White sugar (3 kg) is stirred in a Ross double
13 planetary mixer over a three (3) hour period as set forth in
14 Table 2:

15 Table 2: Preparation of Caramel

16 Time(mins):	0	20	55	115	145	175
17 batch temp (°C)	-	126	150	165	170	176
18 oil temp (°C)	190	190	190	190	195	195
19 mixer speed	1	1	1	6	6	6

20 The product is discharged while warm into Teflon-
21 coated aluminum pans, and after cooling is broken up into
22 small pieces.

23 (c) Preparation of toner concentrate.

24 The products from steps (a) (400 g) and (b) (600 g) are
25 stirred in a Kenwood mixer vessel, electrically heated by
26 means of a tape controlled by a thermocouple set at 160°C.
27 The melt is allowed to cool gradually to 106°C, then the
28 material is discharged and after cooling is pulverized to
29 4.0 µm median diameter. The product is washed with water to
30 remove undissolved caramel, then washed with isopropyl
31 alcohol to remove water, the solvent being finally replaced
32 by Penetack (Penerco) to obtain a 50% n.v.s. concentrate.

33 (d) Preparation of liquid toner.

34 The product from step (c) is diluted to 2% n.v.s. with
35 Isopar L, 300 g of the diluted dispersion is heated to 40°C
36 and is placed in a vessel, subjected to the action of a Ross

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1 Model Lab-ME high shear mixer at room temperature, and an
2 Isopar L solution of 10% by weight ionomer (AClyn 291A,
3 preheated at 115°C, the ionomer constituting 5, 10 or 20% by
4 weight of the toner solids), is slowly added, after which
5 maximum shear is applied for 3 minutes. The dispersion is
6 allowed to equilibrate for 1 hour and to cool to room
7 temperature. Lubrizol 890 is added in an amount of 100 mg
8 charge director per gram of toner solids. The product is
9 then allowed to equilibrate for a further 2 hours, after
10 which time the charging parameters are measured. Results
11 are shown in Table 3.

12 Table 3: Conductivity of Spherical Toner Particles
13 with Lubrizol 890 Charge Director

Run No.	% A291A	particle conductivity
1	0	3
2	5	115
3	10	162
4	20	164

22 Figs. 4 and 5 show SEM electron-micrographs of the
23 toner particles of run 1 and 4 respectively.

24 A calculation of the thickness of the coating based on
25 the percentage of A291A and the measured diameter of the
26 particles shows that the particles of run 1 have a coating
27 of the order of 0.023 micrometers. As can be seen above even
28 such a thin coating (on the average 2-5 times a mono-layer)
29 results in decided improvement in the conductivity, although
30 not in optimal results. This is believed to be due to
31 unevenness of the coating as shown in Fig. 5. It is
32 believed that a thinner, more even coating, even perhaps as
33 thin as a single monolayer, would result in marked
34 improvement of the conductivity.

35 EXAMPLE 3: SPHERICAL TONER PARTICLES

36 The product of step (c) of Example 2 is diluted to 4%
37 n.v.s. with Marcol 82 (Exxon), a highly refined petroleum
38 oil, 300 g of the diluted dispersion is preheated to 40°C,
39 placed in a vessel, subjected to the action of a Ross Model
40 Lab-ME high shear mixer, Marcol 82 solution of 10% by weight

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1 ionomer (AClyn 293A, preheated at 115°C, the ionomer
2 constituting 5% by weight of the toner solids), is slowly
3 added, after which maximum shear is applied for 3 minutes.
4 The mixture is allowed to cool to room temperature and the
5 dispersion is allowed to equilibrate for at least 3 hours.
6 Then aluminum tributoxide (Aldrich) is added in an amount of
7 5 mg per gram of toner solids. After 2 hours, 40 mg per
8 gram of toner solids of either basic barium petronate (BBP,
9 Witco) or calcium petronate (CAP 25H, Witco), are added to
10 the toner. Results in terms of charging parameters are
11 shown in Table 4.

12 Table 4: Conductivity of Spherical Toner Particles
13 with BBP and CAP Charge Directors

14 Charge 15 Director	16 % A293A	17 particle 18 conductivity	19 low field 20 conductivity	21 polarity
22 BBP	23 0	24 1	25 12	26 +
27 CAP	28 0	29 2	30 14	31 -
32 BBP	33 5	34 24	35 6	36 -
37 CAP	38 5	39 17	40 5	41 -

42 Note: Conductivity in pmho/cm

43 The toners containing A293A gave very good copy
44 quality when used in a duplicator, whereas in absence of
45 A293A the copies were unreadable.

46 **EXAMPLE 4: TONER COMPRISING POLYMER WITH BI-AMINO GROUPS**

47 (a) Acryloid DM55 (600 g), an acrylic resin
48 containing tertiary amino groups marketed by Rohm and
49 Haas, is ground cryogenically to form a fine powder, which
50 is then transferred to a 1S attritor (Union Process)
51 together with 1200 g Isopar L. The mixture is ground for 24
52 hours at room temperature, while cooling with water. The
53 resultant particles had a median size of 1.4 μ m.

54 (b) The product of part (a), after appropriate
55 dilution (300 g of 2% n.v.s.) was placed in a vessel,
56 subjected to the action of a Ross Model Lab-ME high shear
57 mixer at 40°C, and an Isopar L solution of 10% by weight
58 ionomer (AClyn 291A, preheated at 115°C, the ionomer

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1 constituting either 10 or 20% by weight of the toner
2 solids), is slowly added, after which maximum shear is
3 applied for 3 minutes. The dispersion is allowed to cool
4 and equilibrate for 1 hour and then Lubrizol 890 is added in
5 an amount of 100 mg charge director per gram of toner
6 solids. The product is then allowed to equilibrate for a
7 further 2 hours, after which time the charging parameters
8 are measured.

9 Results are shown in Table 5, from which it may be
10 seen that use of the ionomer (i) markedly increases the
11 chargeability of the toner particles (by an order of
12 magnitude as seen in the high field conductivity data), with
13 the consequence that the toner is satisfactory for use in an
14 imager, and (ii) reverses the polarity of the toner
15 particles.

16 Table 5: Conductivity of DM55 Toner Particles

Run No.	% A291A	conductivity (pmho/cm)		polarity
		low field	high field	
1	0	5	12	100%(+)
2	10	12	98	100%(-)
3	20	12	115	100%(-)

27 While the present invention has been particularly
28 described, persons skilled in the art will appreciate that
29 many variations and modifications can be made. Therefore,
30 the invention is not to be construed as restricted to the
31 particularly described embodiments, rather the scope, spirit
32 and concept of the invention will be more readily understood
33 by reference to the claims which follow.

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